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## (54) Method of producing Cu - Ag alloy based conductive material.

(57) A method, for producing a Cu - Ag alloy based conductive material containing 10 to 20 at % Ag, comprises the steps of continuously casting the alloy and quickly cooling the rod,cold- working to a reduction in area of 80 % or more, then heat treating at a temperature of 250 to 350 °C for 1 hour or more, and finally cold-working to a reduction in area of 90 % or more as defined based on the cast rod. This makes it possible to produce conductive material having a high strength of 700 MPa or more and conductivity of 75 %IACA or more.



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The present invention relates to a method of producing a Cu - Ag alloy based conductive material employable for high field magnets such as l ng pulse magnets r the like.

In recent years, a variety of re earch, which uses a high intensity of magnetic field, hav be n widely conducted in the fields of physics, engineering, medical science and so forth. Consequently, corresponding development works have been intensively conducted for providing high field magnets. In the circumstances, a Cu - Ag alloy with a high strength and high conductivity has been developed. This material is expected to be utilized as a raw material for a so-called long pulse magnet which generates a very high magnetic field in excess of 80T with a longer duration time of several milliseconds to several ten milliseconds. The long pulse magnet is used for investigating the phenomena of superconductivity.

The conventional Cu - Ag alloy is produced by way of the steps of casting a Cu based alloy containing about 10 to 16 at % of Ag by an ingot casting process, hot-forging the casted ingot at a temperature of 450 °C, intermediate heat treatment at a temperature of 400 °C or 450 °C for 2 to 10 hours, grinding or facing, and finally cold-drawing.

However, it has been found that the conventional conductive Cu - Ag alloy produced in the above-described manner has the following drawbacks.

Since hot-forging can process a small amount of alloy at a time due to a restricted temperature range, heating and forging should be repeated many times. Since flaws are likely to appear on the surface of the alloy during each hot-forging, there arises the necessity for facing the surface, resulting in the low yield and high cost. When producing large ingot aiming a long wire, segregation occurs easily in the casting process, and moreover the casted ingot is liable to crack during hot-forging. Another drawback is difficulty to produce wires with a small diameter. When the ingot casting process is employed, the slow rate of cooling will cause precipitation in the ingot, which leads to a failure in the stable production of the materials with expected conductivity and strength. The drawback appears more remarkably in the production of large size ingots.

The present invention has been made in consideration of the foregoing background.

An object of the present invention is to provide a method of stably producing a conductive material with high strength and high conductivity not only at a reduced cost but also at an improved yielding rate.

According to one aspect of the present invention, there is provided a method of producing a Cu - Ag alloy based conductive material, wherein the method comprises a step of continuously casting a Cu based allow containing 10 to 20 at % of Ag and the balance consisting of Cu and unavoidable impurities and quickly cooling the cast rod at a rate where no precipitation occurs, a step of subjecting the cast rod to cold-working to a reduction in area of 80% or more, a step of subjecting the cold-working rod to heat treatment at a temperature of 250 to 350°C for 1 hour or more, and a step of subjecting the heat-treated rod to cold-working to a reduction in area of 90% or more as defined based on the cast rod.

According to the present invention, a conductive material having a high strength (700 MPa or more in tensile strength) and high conductivity (75 %IACA or more) can be stably produced at high productivity and a lower cost. When the conductive material is employed for high field magnets, a very high intensity of magnetic field can be generated in excess of 80T. Thus, utilization of this material contributes towards the clarification of superconductive phenomena as well as the promotion of basic research activities which need a very high intensity of magnetic field. This material will be also effectively used for lead frame of IC, electrodes, and reinforcement/stabilization of superconductive wires.

Some embodiments of the invention will now be described by way of example with reference to the accompanying drawings, in which:

Fig. 1a is a SEM photograph of the transverse cross-section of an as-cast Cu - Ag alloy produced according to the present invention;

Fig. 1b is a similar cross-section at a higher magnification;

Fig. 2a is a SEM photograph of the transverse cross-section of an as-cast Cu - Ag alloy produced by the conventional method;

Fig. 2b is a similar view at a higher magnification, and

Fig. 3 is a diagram for illustrating the definition of "cooling rate".

In a continuous casting process, the "cooling rate" is defined as the average cooling rate. The average cooling rate, R is represented by the following equation:

$$R\ (°C/Sec.) = \frac{t1 - t2}{\frac{1}{V} \cdot 60}$$

in which t1 is a solidifying temperature (°C), t2 is a temperature in an outlet, 1 is the length from the solidifying point to the outl t f a rod as shown in Fig. 3 and V is the casting speed (mm/min).

Some practical xamples of cooling rates are as follows.

In a case where the rod diameter is 8mm, V = 500 mm/min., 1 = 350mm, t1 = 1100°C, t2 = 100°C and R = 23.8°C/sec.

In a case where the rod diameter is 14mm, V = 300 mm/min., 1 = 350mm, t1 = 1100°C, t2 = 150°C and R = 13.6 °C/sec.

In a case where the rod diameter is 40mm, V = 40 mm/min., 1 = 200 mm, t1 = 1100°C, t2 = 300°C and R = 2.7 °C/sec.

In a case where the rod diameter is 60 mm, V = 20 mm/min., 1 = 200mm, t1 = 1100°C, t2 = 400°C and R = 1.2 °C/sec.

Thus it can be inferred that the rate depends on the diameter of the rod. If the diameter is a maximum of 60mm, the cooling rate is preferably 1 °C/sec or more.

The present invention will now be described in detail by embodiments.

In the present invention, the conductive material produced is produced by using a Cu based alloy containing 10 to 20 at % of Ag and the balance consisting of Cu and unavoidable impurities.

The composition of the alloy is determined such that the product material exhibits an excellent workability in addition to high strength and high conductivity. In detail, if the Ag content is lower than 10 at %, a product material exhibits an insufficient strength. On the contrary, if it exceeds 20 at %, the workability of a product material is degraded while the strength is left substantially unchanged. For this reason, it is preferable that a content of Ag is set to the range from 12 to 18 atomic percentages.

The method of the present invention will be described in detail as follows:

(1) First, a Cu based alloy rod is produced from a raw material mentioned above by a continuous casting process. For the present invention, the cooling rate is very important. It is necessary that the casted rod is cooled at the rate where any precipitation do not occur in the rod. The photograph of scanning electron microscope for the cast structure of rapidly cooled rod is shown in Fig. 1, that of conventional ingot casting process is shown in Fig. 2. As is apparent from these photographs, the cast structure of the Cu - Ag alloy is basically such that an eutectic phase 2 composed of α phase (Cu solid solution) and β phase (Ag solid solution) are uniformly distributed in the matrix of α-phase 1 in a net-shaped pattern surrounding the α phase 1. In the α phase, Ag is dissolved in the high concentration of Cu. in the β phase, Cu is dissolved in the high concentration of Ag. As shown in Fig. 1, no precipitation is recognized in the structure of the Cu - Ag alloy produced by continuous casting with rapid cooling. Further, Fig. 2 shows a number of precipitated particles 3 in the cast structure of the conventional Cu - Ag alloy. The precipitation in this stage makes it difficult to control precipitation during subsequent working and heat treatment, and moreover, there is a possibility that final products do not exhibit enough strength and conductivity. Consequently, rapid cooling in the present invention makes it possible for the Cu - Ag alloy based conductive material to have a high strength and high conductivity. A proper diameter of cased rod is about 5 to about 50 mm. The larger diameter of the rod increases the conductivity in the final properties of product.

(2) Next, the rod-shaped product is subjected to cold- working. The extent of the cold-working is set to 80 % or more, preferably 90 to 95 % in terms of an area reduction rate. If the area reduction rate (= [a cross-sectional area of the rod prior to working - a cross-sectional area of the rod after working] / [a cross-sectional area of the rod prior to working] x 100) is less than 80 %, a strength of a product alloy is reduced.

(3) Subsequently, the wire produced by cold-working is subjected to heat treatment at a temperature of 250 to 350 °C for 1 hour or more. Specifically, the heat treatment time should be 10 hours or more at the temperature of 250 °C, 1 to 10 hours at 300 °C, and 1 to 5 hours at 350 °C. In the case that the heat treatment temperature is lower than 250 °C or the heat treatment time is shorter than 1 hour, the conductivity of a product wire, i.e., one of the final properties is degraded. If the heat treatment temperature is higher than 350 °C, the strength of wire is degraded.

(4) Thereafter, the heat-treated wire is subjected to cold-working to a reduction in area of 90 % or more as defined based on the cast rod, more preferably at 95 to 99 %. In the case of cold working to a reduction in area of less than 90 %, a sufficiently high strength could not be obtained with the wire.

A Cu - Ag conductive material could be produced by way of these steps at high productivity and at a high yield with excellent reproductivity.

In addition, it is found that the strength and the conductivity of a product wire could be improved further by heat treatment at a temperature of 400 to 500 °C for 2 to 50 hours before the step as described in the paragraph (1), i.e., before the cast rod is subjected to cold working. Specifically, the heat treatment time should be 10 to 50 hours at the temperature of 400 °C, 5 to 50 hours at 450 °C, and 2 to 20 hours at 500 °C. It should be noted that an advantageous effect derived from the process could not be obtained if the temperature and time of heat treatment is out of the aforementioned range.

Additi nally, after completi n of step (4) wh n th final diameter of its wire is specified, the conductivity of the wire could be improved with f w reduction of the strength by the heat treatment for 1 hour or more at a temperature of 150 to 300 °C. Specifically, the heat treatment tim should be 5 hours or more at the temperature of 150 °C, 1 to 50 hours at 200 °C, 1 to 20 hours at 200 °C and 1 t 5 hours at 300 °C. If th h at treatment tem-

perature is lower than 150 °C or the heat treatment time is shorter than 1 hour, the conductivity of a product wire could not sufficiently be improved. If the heat treatm nt temperature is higher than 300 °C, the str ngth is remarkably degraded.

When a final product of wire is specified to have a rectangular cross-section, it is desirable to shape the wire in the step (4) after a heat treatment for several hours, e.g., for 1 to 2 hours at a temperature of 250 °C or less.

Next, a few examples of producing a conductive material according to the present invention will be described below.

Example 1

A Cu based alloy containing 16% of Ag and the balance of Cu was continuously casted in the form of a rod with a diameter of 8 mm by use of a horizontal type continuous casting machine which had a graphite mold and a water cooling jacket around the periphery of the graphite mold. In this example, the temperature of molten metal was 1300 °C and the cast rod was quickly cooled. The cast rod was cold drawn until the diameter of a wire was reduced to 2 mm, which corresponded to a reduction in area of 93.8 %. Thereafter, the wire was then heat treated at a temperature of 300 °C for 1 hour. Subsequently, the wire was cold drawn until the diameter of a wire was reduced to 1.2 mm, which corresponded to a reduction in area of 93.8 % as defined based on the cast rod to produce a Cu - Ag alloy based conductive material having a rectangular cross-sectional shape with a thickness of 0.8 mm x a width of 1.2 mm.

Conductivity and a tensile strength of the Cu - Ag alloy based conductive material having a rectangular cross-sectional area were measured at the room temperature. The results are shown in Table 1. It should be noted that conductivity of the Cu - Ag based conductive material was measured by double-bridge method for a length of 300 mm of testpieces each having a length of 400 mm. A tensile strength was measured for the length of 250 mm of the same testpieces with the cross head speed of 10 mm/min by operating a testing machine manufactured by Shimazu Co., Ltd.

Example 2

A Cu - Ag alloy based conductive material having a rectangular cross-sectional shape with a thickness of 0.8 mm x a width of 1.2 mm or a thickness of 4 mm x a width of 6 mm was produced in the same manner as Example 1 with the exception that an outer diameter of each cast rod and heat treatment conditions and cold-working conditions for the cast rod were changed as shown in Table 1.

Conductivity and a tensile strength of the Cu - Ag alloy based conductive material were measured, in the same manner as Example 1. The results are shown in Table 1.

Comparative Examples 1 to 8

Cast rods were produced in the same manner as Example 1. Cu -Ag based alloy conductive materials each having a rectangular cross-sectional shape with a thickness of 0.8 mm x a width of 1.2 mm were then subjected to cold-working using the foregoing cast rods in the same manner as Example 1 with the exception that heat treatment conditions and cold-working conditions for each cast rod were changed as shown in Table 2.

Conductivity and a tensile strength of each testpiece were measured. The results are shown in Table 1.

Comparative Example 9

A Cu based alloy having the same composition as that in Example 1 was cast by employing an ingot casting process to produce cast ingots each having a diameter of 95 mm. Each cast ingot was repeatedly heated and forged several times at a temperature of 450 °C to produce a rod having a diameter of 45 mm, and subsequently, this rod was subjected to planing to obtain a rod with a diameter of 40 mm. Thereafter, the rod was subjected to heat treatment and cold working under operative conditions as shown in Table 1 to produce a Cu - Ag based alloy conductive material having a rectangular cross-sectional shape with a thickness of 4 mm x a width of 6 mm (a reduction in area of 99.7 %).

Conductivity and a tensile strength of the thus obtained Cu - Ag based alloy conductive material were measured. The results are also shown in Table 2.

As is apparent from th results shown in Tables 1 and 2, according to th present invention, Cu - Ag all y based conductive material each having a high strength and excellent conductivity employable for high field magnets can b produced at high productivity and at an improved yield whil maintaining excellent reproductivity.

TABLE 1

| | | PRODUCTION PROCESS AND WORKING CONDITIONS | | | | | | *1 | | PROPERTIES | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | DIAMETER OF CAST ROD (mm) | HEAT TREATMENT (℃×hr) | COLD WORKING (mm IN DIAMETER) (REDUCTION) | HEAT TREATMENT (℃×hr) | COLD WORKING (mm IN DIAMETER) (REDUCTION) | HEAT TREATMENT (℃×hr) | COLD WORKING (mm IN DIAMETER) (REDUCTION) | HEAT TREATMENT (℃×hr) | TENSILE STRENGTH (MPa) | CONDUCTIVITY (%IACS) |
| EXAMPLES | 1 | 8 | | → 2.0 (93.8%) | 300×1 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 940 | 76 |
| | 2 | 8 | | → 2.0 (93.8%) | 300×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 930 | 77 |
| | 3 | 8 | | → 2.0 (93.8%) | 300×5 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 920 | 78 |
| | 4 | 8 | | → 2.0 (93.8%) | 350×1 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 900 | 79 |
| | 5 | 8 | | → 2.0 (93.8%) | 350×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 890 | 80 |
| | 6 | 8 | | → 2.0 (93.8%) | 350×5 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 820 | 83 |
| | 7 | 40 | | → 10 (93.8%) | 300×5 | → 5.8 (97.9%) | 250×2 | → 4×6 (98.1%) | | 900 | 78 |
| | 8 | 40 | | → 10 (93.8%) | 300×5 | → 5.8 (97.9%) | 250×2 | → 4×6 (98.1%) | 250×2 | 850 | 82 |
| | 9 | 8 | 450×10 | → 2.0 (93.8%) | 300×1 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 1120 | 74 |
| | 10 | 8 | 450×10 | → 2.0 (93.8%) | 300×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 1110 | 74 |
| | 11 | 8 | 450×10 | → 2.0 (93.8%) | 300×5 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 1070 | 75 |
| | 12 | 8 | 450×10 | → 2.0 (93.8%) | 350×1 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 1060 | 75 |
| | 13 | 8 | 450×10 | → 2.0 (93.8%) | 350×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 1020 | 76 |
| | 14 | 8 | 450×10 | → 2.0 (93.8%) | 350×5 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 960 | 80 |
| | 15 | 8 | 450×10 | → 10 (93.8%) | 350×2 | → 5.8 (97.9%) | | → 4×6 (98.1%) | | 1010 | 79 |
| | 16 | 8 | 450×10 | → 10 (93.8%) | 350×2 | → 5.8 (97.9%) | | → 4×6 (98.1%) | 250×1 | 980 | 83 |

* 1 : THE REDUCTION IN AREA BASED ON THE DIAMETER OF A CAST ROD.

TABLE 2

| | | PRODUCTION PROCESS AND WORKING CONDITIONS *1 | | | | | | | | PROPERTIES | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | DIAMETER OF CAST ROD (mm) | HEAT TREATMENT (℃×hr) | COLD WORKING (mm IN DIAMETER) (REDUCTION) | HEAT TREATMENT (℃×hr) | COLD WORKING (mm IN DIAMETER) (REDUCTION) | HEAT TREATMENT (℃×hr) | COLD WORKING (mm IN DIAMETER) (REDUCTION) | HEAT TREATMENT (℃×hr) | TENSILE STRENGTH (MPa) | CONDUCTIVITY (%IACS) |
| COMPARATIVE EXAMPLES | 1 | 8 | | → 1.2 (97.8%) | | | | → 0.8×1.2 (98.1%) | | 880 | 70 |
| | 2 | 8 | | → 2.0 (93.8%) | 150×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 900 | 70 |
| | 3 | 8 | | → 2.0 (93.8%) | 200×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 920 | 70 |
| | 4 | 8 | | → 2.0 (93.8%) | 450×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 680 | 86 |
| | 5 | 8 | 450×10 | → 2.0 (93.8%) | | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 1150 | 71 |
| | 6 | 8 | 450×10 | → 2.0 (93.8%) | 150×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 1160 | 71 |
| | 7 | 8 | 450×10 | → 2.0 (93.8%) | 200×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 1165 | 71 |
| | 8 | 8 | 450×10 | → 2.0 (93.8%) | 400×2 | → 1.2 (97.8%) | | → 0.8×1.2 (98.1%) | | 690 | 85 |
| | 9 | 40 (*2) | 450×15 | → 5.84 (99.6%) | | | 300×2 | → 4×6 (99.7%) | | 870 | 81 |

* 1 : THE REDUCTION IN AREA BASED ON THE DIAMETER OF A CAST ROD.

* 2 : INGOT CASTING (95 mm IN DIAMETER) → HOT FORGING AT 450 ℃ (45 mm IN DIAMETER) → FACING (40 mm IN DIAMETER)

## Claims

1. A method of producing a Cu - Ag alloy based conductive material containing 10 at % to 20 at % of Ag and the balance consisting of Cu and unavoidable impurities, comprising the steps of:
   (a) continuously casting a Cu based alloy containing 10 at % to 20 at % of Ag and quickly cooling the cast rod at a rate where no precipitation occurs;
   (b) subjecting the rod to cold-working to a reduction in area of 80 % or more;
   (c) subjecting the rod to heat treatment at a temperature of 250°C to 350°C for 1 hour or more; and
   (d) subjecting the rod to cold-working to a reduction in area of 90% or more as defined based on the cast rod.

2. The method of claim 1, wherein the cold-worked rod is subjected to a further step (e) of heat treatment at a temperature of 150°C to 300°C.

3. The method of claim 1, wherein a content of Ag is 12 at % to 18 at %.

4. A method of producing a Cu - Ag alloy based conductive material containing 10 at % to 20 at % of Ag and the balance consisting of Cu and unavoidable impurities, comprising the steps of:
   (a) continuously casting a Cu based alloy containing 10 at % to 20 at % of Ag and the balance consisting of Cu and unavoidable impurities and quickly cooling the cast rod at a cooling rate which does not cause precipitation;
   (b) subjecting the rod to heat treatment at a temperature of 400°C to 500°C for 2 hours to 50 hours;
   (c) subjecting the rod to cold-working to a reduction in area of 80 % or more;
   (d) subjecting the rod to heat treatment at a temperature of 250°C to 350°C for 1 hour or more; and
   (e) subjecting the rod to cold-working to a reduction in area of 90% or more as defined based on the cast rod.

5. The method of claim 4, wherein the cold-worked rod is subjected to a further step (f) of heat treatment at a temperature of 150°C to 300°C for 1 hour.

6. The method of claim 4, wherein the content of Ag is 12 at % to 18 at %.

7. A Cu - Ag alloy produced by the method of any preceding claim and suitable for use as a high field magnet.

FIG. 1(a)

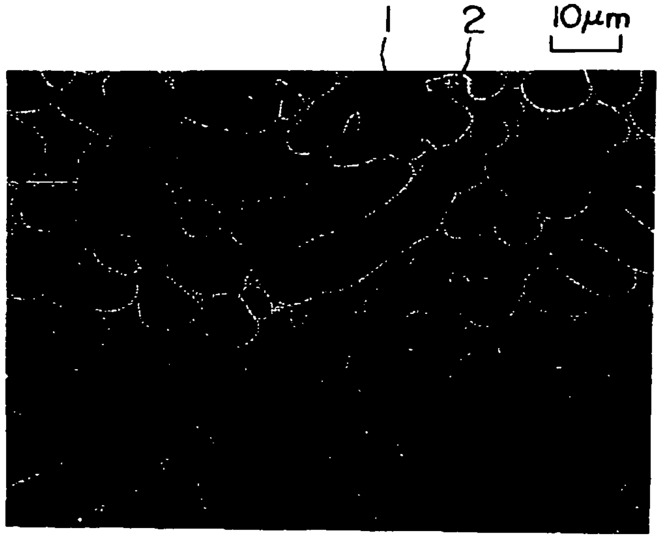



FIG. 1(b)

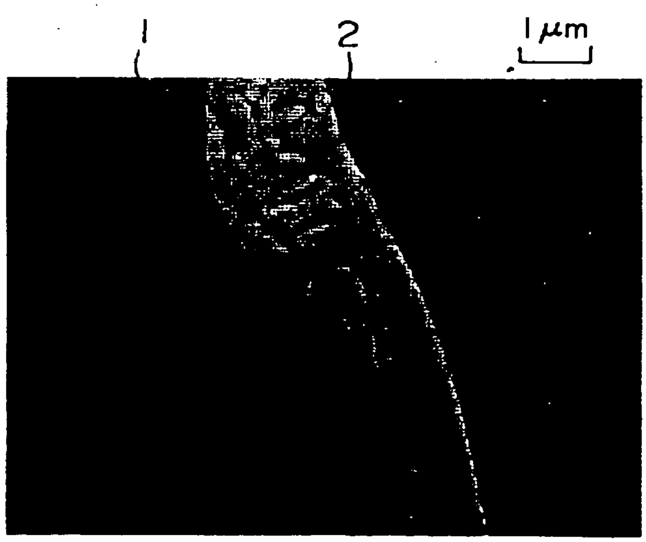


FIG. 2(a)

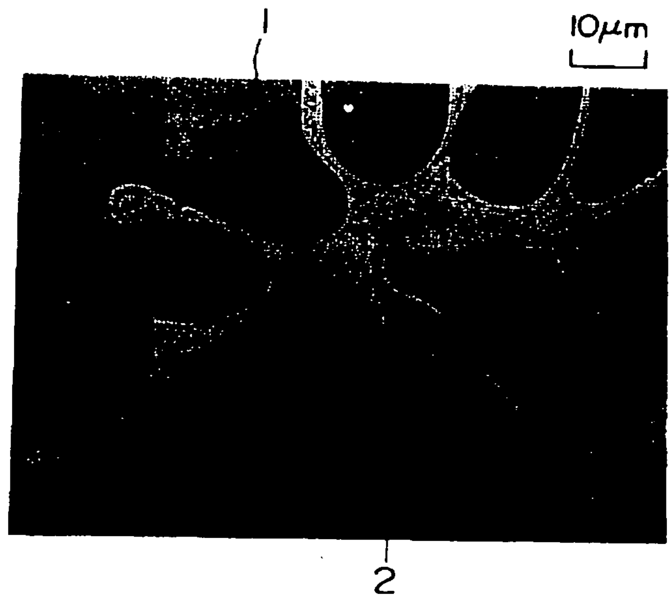



FIG. 2(b)

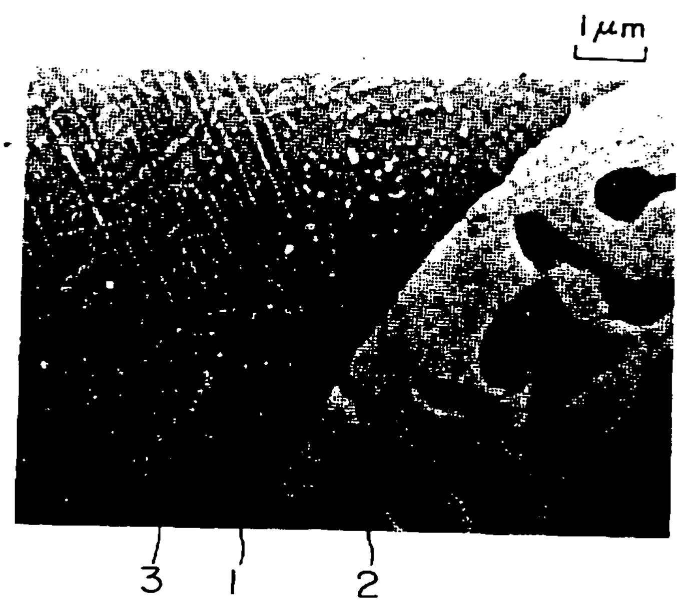
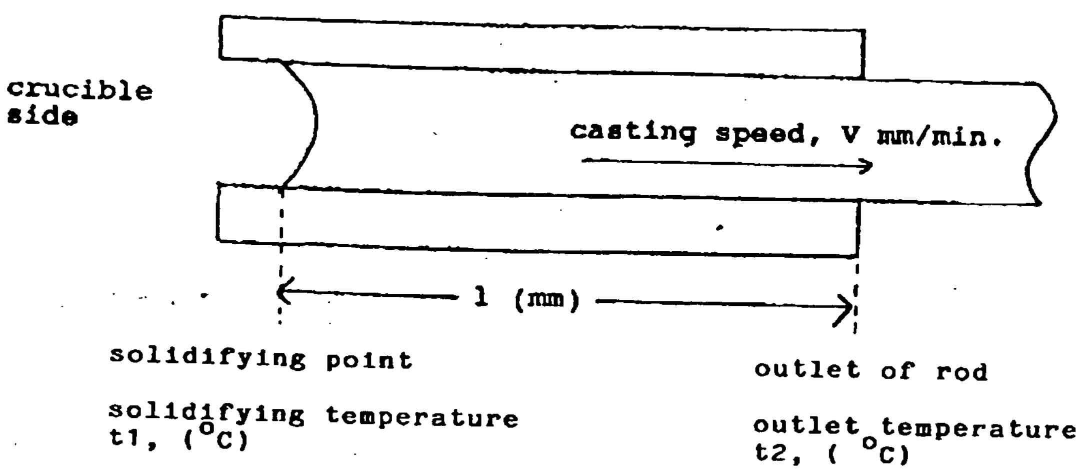


FIG 3


crucible side
casting speed, V mm/min.
l (mm)
solidifying point
solidifying temperature t1, (°C)
outlet of rod
outlet temperature t2, ( °C)

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 93 30 7254

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|---|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| Y | APPL. PHYS. LETT. vol. 59, no. 23, 2 December 1991, pages 2965 - 2967 SAKAI Y., INOUE K., ASANO T., WADA H. AND MAEDA H. * whole document * | 1-7 | C22F1/08 C22C9/00 |
| Y | PATENT ABSTRACTS OF JAPAN vol. 16, no. 375 (C-0973)12 August 1992 & JP-A-41 20 227 ( NATL. RES. INST. FOR METALS ) * abstract * | 1-7 | |
| Y | PATENT ABSTRACTS OF JAPAN vol. 9, no. 228 (C-303)15 May 1985 & JP-A-60 086 227 ( FUJIKURA DENSEN KK ) * abstract * | 1-7 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| | | | C22F C22C |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| MUNICH | 14 JANUARY 1994 | P.PIVALICA-BJÖRK |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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